

Doping of graphene adsorbed on the a-SiO₂ surface

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We have performed an *ab initio* theoretical investigation of graphene sheet adsorbed on amorphous SiO₂ surface (G/a-SiO₂). We find that graphene adsorbs on the a-SiO₂ surface through van der Waals interactions. The inhomogeneous topology of the a-SiO₂ clean surface promotes a total charge density displacement on the adsorbed graphene sheet, giving rise to electron-rich as well as hole-rich regions on the graphene. Such anisotropic distribution of the charge density may contribute to the reduction of the electronic mobility in G/a-SiO₂ systems. Furthermore, the adsorbed graphene sheet exhibits a net total charge density gain. In this case, the graphene sheet becomes n-type doped, however, with no formation of chemical bonds at the graphene-SiO₂ interface. The electronic charge transfer from a-SiO₂ to the graphene sheet occurs upon the formation of a partially occupied level lying above the Dirac point. We find that such partially occupied level comes from the three-fold coordinated oxygen atoms in the a-SiO₂ substrate.

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Considerable progress has been made addressing the electronic and structural properties of graphene, however, the development of nanodevices based on graphene is still in its infancy. Graphene is a semiconductor material with zero energy bandgap. The valence and the conduction bands are connected through a linear energy-momentum relation at the K points lying at the corners of the hexagonal Brillouin zone (Dirac points) [1]. The very high electronic mobility, up to 200,000 cm²/(V.s), makes graphene a quite suitable material to the development of new electronic (nano)devices. Indeed, there are experimental realizations of field effect transistors (FETs) based on graphene sheets [2–6]. In those systems, SiO₂ has been used as the gate dielectric material. Lemme *et al.* [2] verified a reduction of the electron mobility upon the graphene interaction with the SiO₂ gate, while Romero *et al.* [6] obtained a n-type doping for graphene in contact with a SiO₂ gate. In this case, the authors attributed the presence of surface states to the electronic charge transfer from SiO₂ to the graphene sheet. In contrast, there are experimental results indicating a p-type doping for graphene on SiO₂ gate [7, 8]. Very recently n- and p-type doping of graphene, lying on SiO₂ substrate, has been tuned through a suitable graphene-SiO₂ “interface engineering” [9], where foreign molecules have been placed between the graphene sheet and the SiO₂ surface. Indeed, there are experimental and theoretical studies addressing “interface engineering” applied to modify the electronic and structural properties of carbon nanotubes adsorbed on SiO₂ [10] as well as on the other semiconductor surfaces like Si(001) [11] and InAs(111) [12].

The most of the experimental results indicate that there are no covalent bonds between the graphene sheet and the amorphous SiO₂ substrate (a-SiO₂). It has been suggested a physisorption process [13–15] where van der Waals (vdW) interactions play an important role. Graphene sheet feels the corrugations of the a-SiO₂ surface, giving rise to electron-rich as well as hole-rich regions on graphene, so called “electron-hole puddles” [16]. Based upon the aforementioned findings, the understanding of the electronic and the energetic properties, within an atomic scale, of graphene on a-SiO₂ surface is a important issue to the examined by using *ab initio* total energy calculations.

In this letter we present *ab initio* calculations of graphene adsorbed on the a-SiO₂ surface, G/a-SiO₂. The calculations were performed within the density functional theory (DFT) including the long-range vdW interactions. Our total energy results reveal that vdW interactions rule the graphene adsorption on the a-SiO₂ surface. The inhomogeneous topology of a-SiO₂ gives rise to electron-rich and hole-rich regions on the adsorbed graphene sheet, in accordance with the experimentally observed “electron-hole puddles” for graphene lying on a-SiO₂. However, there is a net charge density gain on the graphene sheet. The electronic charge transfer from a-SiO₂ to graphene occurs due to the formation of a partially occupied state above the Dirac point. We find that such partially occupied state is attributed to the formation of three-fold coordinated O atoms within a-SiO₂.

The amorphous structure was generated through *ab initio* molecular dynamics (MD) simulations based on the

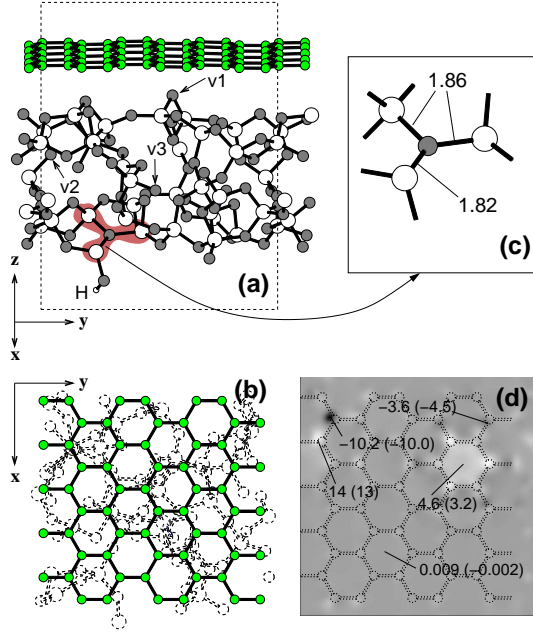


FIG. 1: Atomic structure of graphene adsorbed a-SiO₂ surface, G/a-SiO₂ (a) side-view, (b) top-view, details of the equilibrium geometry of O_{three-fold} (c). In (a) the bottommost O dangling bond was saturated by a H atom and the dashed region indicate a periodic unit cell. In (c) the atomic distances are in Å. Filled (Empty) circles represent the O (Si) atoms. (d) Total charge density fluctuation ($\Delta\rho$) within a region of ± 0.5 Å with respect to the (equilibrium) vertical position of the n-type doped graphene sheet. Within the parentheses we present $\Delta\rho$ for the neutral G/a-SiO₂ graphene sheet. $\Delta\rho$ is in unit of $10^{14}e/\text{cm}^2$.

DFT approach as implemented in the VASP code [17–19]. Initially we obtained the a-SiO₂ bulk phase. We have used a supercell with 96 atoms and we made a suitable choice of the lattice constants of the supercell, 12.47 and 12.96 Å along the x and y directions, respectively, in order to match with the calculated equilibrium lattice constant of an isolated graphene sheet (Fig. 1). While the supercell volume was minimized along the z direction, thus, avoiding any artificial strain in the a-SiO₂ bulk. We next include a vacuum region of ~ 12 Å parallel to the z direction, within the slab method, and then we repeat the MD simulations in order to get an a-SiO₂ clean surface. In Ref. [20] we present details on the generation procedure of amorphous SiO₂ bulk structure. Once we obtained a well described a-SiO₂ surface, we start to investigate the equilibrium geometry, energetic stability, and the electronic properties of a graphene sheet adsorbed onto a-SiO₂ surface. Here the calculations were performed by using the DFT approach as implemented in the SIESTA code [21]. The generalized gradient approximation due to Perdew, Burke and Ernzerhof (PBE) [22] was used, and the van der Waals interaction was described within a semiempirical approach, following the Grimme formula [23]. The electron-ion interactions were calculated by using norm-

conserving pseudopotentials [24]. All the atomic positions of the G/a-SiO₂ system were relaxed by using the conjugated gradient scheme, within a force convergence criterion of 20 meV/Å.

Figure 1(a) presents the structural model for the physisorbed G/a-SiO₂ system, where we have considered nine G/a-SiO₂ configurations on two different a-SiO₂ surface structures. At the equilibrium geometry we find a graphene – a-SiO₂ equilibrium vertical distance ($d_{\text{G-SiO}_2}$) of 3.64 (3.30) Å for an a-SiO₂ surface corrugation of 1.7 (1.5) Å [25]. Although the relatively short distance between the graphene sheet and the topmost O atoms, we do not find the formation of C–O chemical bonds. The strength of graphene adsorption on a-SiO₂ can be measured by comparing the total energies of the isolated systems, *viz.*: graphene sheet and a-SiO₂ surface, with the total energy of the graphene adsorbed system, G/a-SiO₂. We find that the formation of G/a-SiO₂ is an exothermic process with an adsorption energy (E^{ads}) of 6.3 ± 0.4 meV/Å². Our adsorption energy and equilibrium geometry results are in good agreement with the experimental estimative of Ishigami *et al.*, $E^{\text{ads}} = 6$ meV/Å², and $d_{\text{G-SiO}_2} = 4.2$ Å [14]. Recent theoretical calculations, within the DFT-LDA approach with no inclusion of vdW interactions, obtained $E^{\text{ads}} = 1$ meV/Å² and $d_{\text{G-SiO}_2} = 3.6$ Å for graphene on a-SiO₂ [6]. In contrast, other experimental measurements obtained $d_{\text{G-SiO}_2}$ of 5.8 Å for G/a-SiO₂, which may indicate the presence of foreign elements at the G–SiO₂ interface [8]. We next calculate E^{ads} by turning off the vdW contribution from our total energy results. In this case, the formation of G/a-SiO₂ becomes no longer exothermic, $E^{\text{ads}} = -0.4$ meV/Å². Thus, showing that graphene sheet adsorbs on a-SiO₂ is mediated by vdW interactions.

Recent experimental findings indicate a corrugation of ~ 5 Å on the a-SiO₂ surface, for a lateral scale of ~ 100 Å [13]. Meanwhile in Ref. [14] the authors suggest that the corrugation of the adsorbed graphene sheet should correspond to around 60% of the one of the a-SiO₂ surface. They measured a graphene corrugation of 1.9 Å and estimate a deformation energy of 1 meV/Å². We obtained a very small corrugation (up to 0.3 Å) and deformation energy (0.7 meV/Å²) for the adsorbed graphene sheet, whereas our simulated a-SiO₂ surface exhibits a corrugation of ~ 1.6 Å. Here we would be able to describe the corrugation of G/a-SiO₂ in a suitable way by increasing the size of the surface unit cell, and performing an additional total energy minimization of the surface area. In this case, we may find higher values of E^{ads} , since the graphene–SiO₂ contact area will increase, however, such increase of E^{ads} will be limited by the induced strain energy upon the deformation of the graphene sheet.

It is worth to note that graphene adsorbed on a-SiO₂ exhibits a quite different picture when compared with graphene on α -quartz. In the latter, due to the presence of oxygen dangling bonds, there is the formation of C–O chemical bonds (with $E^{\text{ads}} = 300$ meV/Å²) on the

O-terminated surface [26]. In addition, it has been suggested a p-type doping of the adsorbed graphene sheet. Whereas in a-SiO₂, which also exhibits an O-rich surface [Fig. 1(a)], we do not find the formation C–O chemical bonds. In our simulated annealing process all the surface O atoms become twofold coordinated, suppressing the (energetically unfavorable) O dangling bonds. Very recent DFT-LDA calculations indicate that the graphene interaction with the (0001) surface of α -quartz is weak, with no C–O chemical bonds [27].

Figure 1(d) depicts the net charge density displacement ($\Delta\rho$) on the adsorbed graphene sheet. $\Delta\rho$ can be written as,

$$\Delta\rho = \rho[\text{G/SiO}_2] - \rho[\text{G}].$$

Where $\rho[\text{G/SiO}_2]$ and $\rho[\text{G}]$ represent the planar averaged total charge density of the adsorbed (G/a-SiO₂) and isolated graphene sheets, respectively. The planar average was performed by considering a region of 0.5 Å above and below the graphene sheet. The last term, $\rho[\text{G}]$, was calculated keeping the same equilibrium geometry as that of G/a-SiO₂. We find graphene regions with $\Delta\rho > 0$ as well as $\Delta\rho < 0$, electron- and hole-rich regions, respectively. Thus, Fig. 1(d) indicates that there is a total charge density fluctuation on the graphene sheet, being in accordance with the recent experimental verification of “electron-hole puddles” in G/a-SiO₂ systems [16, 28]. Here we can infer that the inhomogeneous a-SiO₂ surface topology rules the total charge density fluctuation of the adsorbed graphene sheet. Such fluctuation on the electronic charge density distribution on the graphene sheet should play an important role on the experimentally verified reduction of the electronic mobility for graphene lying on a-SiO₂ surface [2].

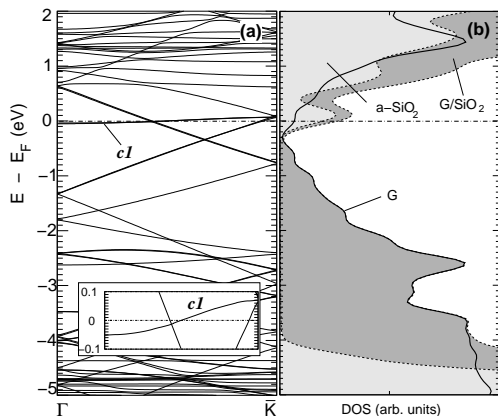


FIG. 2: Electronic band structure (a) and the projected density of states (b) of G/SiO₂ system. Dark shaded regions indicate the total density of states, and the light shaded region indicate the projected density of states of a-SiO₂ surface, and the solid line indicates the projected density of state of (adsorbed) graphene sheet. The inset in (a) present the energy dispersion of the partially occupied level *c1*.

There is a net electronic charge density gain of about

$3 \times 10^{13} \text{ e/cm}^2$, Fig. 1(d), thus, indicating a n-type doping on the adsorbed graphene sheet. Our electronic band structure calculation, Fig. 2(a), confirms statement above. The shape of the Dirac cone has been maintained, since the graphene sheet weakly interacts with the a-SiO₂ substrate. Due to the electronic charge transfer from a-SiO₂ to the graphene sheet, the Dirac point lies below the Fermi energy (E_F). The n-type doping occurs due to the presence of a partially occupied state (*c1*) below the conduction band minimum (CBM) pinning the Fermi level above the Dirac point, see inset of Fig. 2(a). Figure 2(b) presents the density of states (DOS) of G/a-SiO₂ (gray region), and separately the contribution from the adsorbed graphene sheet (solid line), and the a-SiO₂ surface (light gray region). We find, in contrast with previous investigations [6], that *c1* comes from the formation of three-fold coordinated O atoms ($O_{\text{three-fold}}$) in a-SiO₂. Those $O_{\text{three-fold}}$ sites may occur when we have a slightly high local concentration of Si atoms or nearby oxygen vacancies in a-SiO₂ [29–32]. The Si– $O_{\text{three-fold}}$ bond lengths (1.82–1.86 Å) are stretched in comparison with the ones of the two fold coordinated O atoms, ~ 1.66 Å, Fig. 1(c). Those larger bond lengths reduce the binding energy of the electronic states along Si– $O_{\text{three-fold}}$, giving rise to the partially occupied state, *c1*, just below the CBM and pinning the Fermi level. We find that the electronic states of *c1* are localized on the Si atoms nearby $O_{\text{three-fold}}$. In order to verify the adequacy of the proposed origin of *c1*, we calculate the electronic structure of G/a-SiO₂ by suppressing the presence of $O_{\text{three-fold}}$, *i.e.* we have only two fold coordinated O atoms within the a-SiO₂ slab. In this case, we do not find the formation of *c1*, and the Dirac point lies on the Fermi level. That is, the adsorbed graphene sheet becomes neutral. Those results support the proposed role of $O_{\text{three-fold}}$ on the non-covalent n-type doping of graphene on a-SiO₂ substrate. It is worth to note that, for the neutral graphene sheet, we find the same picture for the electron- and hole-rich regions, as depicted in Fig. 1(d), however with different values of $\Delta\rho$. The total charge density fluctuation on the neutral graphene is about 25% smaller in comparison with the (n-type) doped ones.

Finally, we have considered the presence of oxygen vacancies (O_V) in a-SiO₂. We have examined three plausible O_V configurations, on the topmost surface site, and on the subsurface sites, indicated as V1–V3 in Fig. 1(a), respectively. We verify that those vacancies do not give rise to a donor level on the a-SiO₂ surface. For V1 and V2 we find the formation of Si-dimers on the surface (Si–Si bond length of 2.24 Å) inducing the formation of occupied (empty) electronic states near the valence (conduction) band maximum (minimum). Whereas V3 gives rise to a deep occupied state within the a-SiO₂ bandgap.

In conclusion, we find that vdW interactions rules the graphene adsorption on the a-SiO₂ surface. Through a charge density map on the adsorbed graphene sheet we verify that the inhomogeneous a-SiO₂ surface topology promotes an electronic charge density displacement on

the graphene, giving rise to the experimentally verified “electron-hole puddles” [16, 28]. Such electron-rich and hole-rich regions should contribute to the experimentally verified reduction on the electronic mobility of graphene sheets lying on a-SiO₂ surfaces. We find a net charge density gain on the adsorbed graphene sheet, thus, characterizing a n-type non-covalent doping on the graphene. The electronic charge transfer from a-SiO₂ to the graphene sheet comes from the formation of a partially occupied state above the Dirac point, which is attributed to the formation of three-fold coordinated oxygen atoms in a-SiO₂. Those three-fold coordinated oxygen atoms may

occurs upon slightly high local concentration of Si atoms or nearby oxygen vacancies.

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